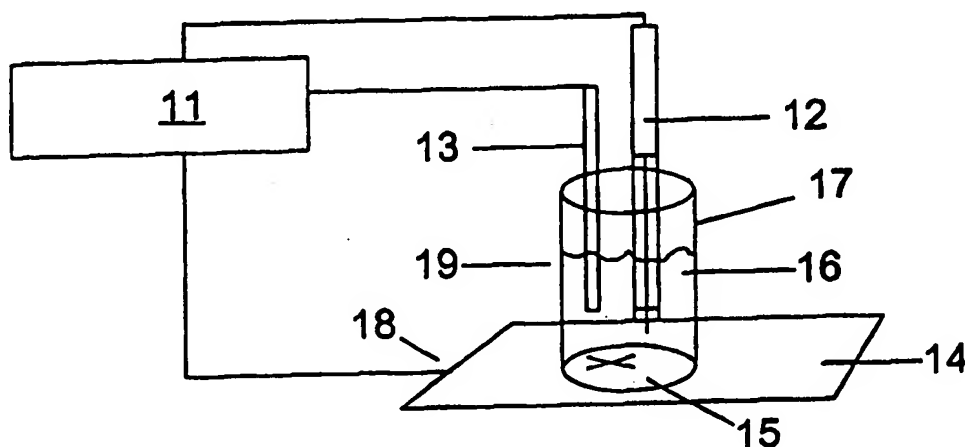




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 27/26	A1	(11) International Publication Number: WO 98/50788
		(43) International Publication Date: 12 November 1998 (12.11.98)
(21) International Application Number: PCT/US98/09766	(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 7 May 1998 (07.05.98)		
(30) Priority Data: 08/852,649 7 May 1997 (07.05.97) US		
Published With international search report.		
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(54) Title: ELECTROCHEMICAL TEST FOR MEASURING CORROSION RESISTANCE



(57) Abstract

The resistance to corrosion of a metal article (14) coated with a resinous coating can be determined by an electrochemical test method which comprises: (a) making a portion of the coated metal article, from which a portion (15) of the coating has been removed to allow for the ultimate passage of electrical current therethrough, the working electrode (18) in an electrochemical cell (19) which also contains a reference electrode (12), a counter-electrode (13) and an electrolytic solution (16); (b) impressing a series of direct current electrical potentials upon the working electrode to enable current to flow between the metal article in the electrochemical cell and the counter-electrode; and (c) measuring the current flow as the direct current potential is varied relative to the reference electrode.

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ELECTROCHEMICAL TEST FOR MEASURING CORROSION RESISTANCEBackground of the Invention

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The use of various electrochemical techniques to quantify the corrosion of a metal article or to measure the effectiveness of a given corrosion inhibition technique has been described in a number of references including the following: H. P. Hack, "The Potentiostatic Technique for Corrosion Studies", p. 57 in Electrochemical Techniques for Corrosion Engineering, R. Baboian, ed., National Association of Corrosion Engineers, Houston 1986; J. R. Scully, Corros. Tests Standard 75-90. (R. Baboian, ed.) American Society for Testing and Materials: Philadelphia, PA, 1995 (CAS Ref.: 125:259468); and G. R. Cameron et al., Electrochemical Techniques for Corrosion Engineering., p. 183.

Such techniques divide broadly into those which interrogate the chemistry of metal and those which interrogate the integrity of the organic coating. Despite the widespread use of organic or resinous coatings to protect corrosion-prone metals, such as steel and aluminum, from deterioration, it has not been standard practice to interrogate electrochemically or otherwise a metal substrate beneath an organic coating. Several recently reported methods are generally relevant to the method described herein without being suggestive thereof: electrochemical noise spectroscopy has been adapted to study underpaint corrosion (L. Meszaros et al., FATIPEC Congr., 22nd(Vol. 4), 68-71, 1994 (CAS Ref.: 124:12877)); measurement of the corrosion resistance of painted metal (M-H Khireddine, Mater. Tech. (Paris) 84, 3-8, 1996 (CAS Ref.: 125:174734)); the use of electrochemical impedance spectroscopy (EIS) for evaluation of underpaint corrosion is widely reported (P. L. Bonora et al., Electrochim. Acta 41, 1073, 1996; F. Mansfield, ACH - Models Chem., 132, 619, 1995 (CAS Ref.: 124:63152)); and EIS has also been adapted for measurement of the corrosion

rates of uncoated steel alloys (A. Nishikata et al., Corros. Sci. 37, 2059, 1995 (CAS Ref.: 124:62557)). EIS is more commonly used to evaluate the integrity of paint coatings on metal substrates by analyzing the coating as an element in an electronic circuit. Reviews of the use of EIS for the evaluation of coatings can be found in the following publications: G.W. Walter, Corrosion Science 1986, 26, 681; and F. Geenan, National Technical Information Service (Order No. PB2-133479).

An electrochemical method for measurement of the barrier resistance of organic coatings (A. Metrot et al., J. Appl. Electrochem. 26, 361, 1996 (CAS Ref.: 124:273062) is also relevant to but distinct from the method described herein.

Summary of the Invention

The present invention is an electrochemical test method for determining the resistance to corrosion of a metal article coated with a resinous coating which comprises: (a) making a portion of the coated metal article, from which a portion of the coating has been removed to allow for the ultimate passage of electrical current therethrough, the working electrode in an electrochemical cell which also contains a reference electrode, a counter-electrode and an electrolytic solution; (b) impressing a series of direct current electrical potentials upon the working electrode to enable current to flow between the metal article in the electrochemical cell and the counter-electrode; and (c) measuring the current flow as the direct current potential is varied relative to the reference electrode.

Description of the Drawings

The present invention is further illustrated by the Drawings, which form a portion of the present specification, wherein;

Fig. 1 is a schematic view of the preferred apparatus for practice of the present invention;

Fig. 2 is an ideal potentiodynamic scan for an active-passive metal; and

5 Fig. 3 is an actual potentiodynamic scan for coated metal in accordance with the present invention.

Description of the Preferred Embodiments

This invention concerns the use of a DC potentiodynamic method, which has been largely used in the development and
10 characterization of uncoated metals and alloys (E. D. Verink, Jr., Electrochemical Techniques for Corrosion Engineering, p. 111), to the measurement of metals coated with an organic or resinous coating in a novel manner. The aforementioned
15 reference to A. Metrot et al. in the section dealing with the background of the present invention, although being used with coated metal test specimens, measured the barrier resistance of the coating in a nondestructive manner without measuring the capability of the coating to passivate areas from which
20 the coating had been removed.

It is proposed that this method is useful in predicting and quantifying the effectiveness of organic coatings applied for the purpose of corrosion protection of metal including the circumstance in which a portion of the coating has been
25 removed from the metal substrate. In the preferred practice of this invention, substrate metal coated with a corrosion-preventing coating and optionally topcoat is made to be the working electrode of an electrochemical cell; a range of increasingly positive electric potentials relative to a
30 reference is imposed on the working electrode (coated substrate), and currents between the working electrode and an inert counter-electrode, corresponding to the various potentials, are measured. The current-voltage curve generated in this manner is highly instructive of the corrosion-

preventing and particularly the passivating capability of the coating.

The use of this technique relies on the possibility of electrical current between working and counter electrodes. To the extent that an organic or resinous coating is electrically insulating and without defect, a coated metal substrate cannot be evaluated with this method. However, no coating is without defect; consequently, this method can be practiced as described. In a preferred embodiment, a score mark or pinhole defect through the coating and exposing bare metal may be made by means of a knife or drill prior to measurement of the current-voltage curve.

Fig. 1 provides a schematic view of a particular apparatus which can be used to practice the current method. Commercially available electrochemistry measuring apparatus of this type that have been used to test uncoated metal specimens and are available, for example, from Gamry Instruments, Inc. (the CMS 105 DC Corrosion Measurement System). As Fig. 1 herein depicts, a potentiostat 11, reference electrode 12, counter-electrode 13, and coated metal sample 14 are provided with a scratched portion 15 of the metal sample 14 residing in an electrolyte solution 16 contained in a suitable non-conductive container 17 which is preferably made of glass.

The electrochemical test method for determining the resistance to corrosion of the coated metal article 14 comprises: making a portion of that coated metal article, from which a portion 15 of the coating has been removed to allow for the ultimate passage of electrical current therethrough, the working electrode 18 in an electrochemical cell 19 which also contains a reference electrode 12, a counter-electrode 13 and an electrolytic solution 16; impressing a series of direct current electrical potentials upon the working electrode 18 to enable current to flow between the metal article in the electrochemical cell 19 and the counter-electrode 13; and measuring the current flow as

the direct current potential is varied relative to the reference electrode. In the present method, the working electrode is always the coated metal article under test, but the reference and counter-electrodes can be varied, if
5 desired. Representative reference electrodes include the saturated calomel, normal hydrogen, and platinum electrodes, while the counter-electrode can be a graphite or platinum electrode.

Figs. 2 and 3 illustrate, respectively, the type of
10 potentiodynamic scan for uncoated metal (as illustrated by M.G. Fontana et al., Corrosion Testing, 1986, Figure 9-25) and for coated metal in accordance with the present invention. In Fig. 2 the transpassive region of the scan is represented by reference numeral 21, with the passive and active regions of
15 the scan being represented by 22 and 23, respectively.

Using the ideal plot of Fig. 2 as a model, the experimental scan depicted in Fig. 3 can be evaluated to determine a sample's potential resistance to corrosion. In Fig. 3, E_{M/M^+} represents the open circuit potential and $i_{o, M/M^+}$
20 represents the open circuit current characteristic of the sample. At potentials near E_{M/M^+} the metal follows typical Tafel behavior with the rate of dissolution of the metal increasing exponentially with increased potential applied to the sample. This is the active region (labeled "A" in Fig.
25 3). At positive potentials (anodic) of the open circuit potential, there is oxidation of the metal. In the depicted apparatus, the rate of oxidation of the metal is proportional to the current density. An active-passive metal is characterized by E_{pp} , the primary passive voltage and a
30 corresponding I_c , the critical anodic current density for passivity. The point where current density begins to decrease with increasing potential is the active-passive transition of the sample under test. The decrease in current density is thought to result from formation of an insulating oxide film
35 on the metal surface. In the passive region (labeled "P" in

Fig. 3), the current (rate of corrosion of the metal) decreases to some value which is relatively constant and is characteristic of the passivity of the sample under test. The transpassive region (labeled "TP" in Fig. 3), where the rate of dissolution of metal again increases with increasing potential at high anodic potentials, is thought to result from destruction of the metal's protective oxide layer.

The present invention is further illustrated by the Examples which follow.

Example 1

This Example illustrates the coating of aluminum coupons with poly(2,6-dimethylphenol) and comparing the DC potentiodynamic behaviors of coated and uncoated coupons.

Unpretreated aluminum coupons (designated "ACT aluminum 6061T6 03x06x032 cut only; unpolish") were obtained from ACT Laboratories, Inc., Hillsdale, MI 49242-0735 and were cleaned with acetone and methylethylketone (MEK) scrubbing. A coating solution was formed by blending 10 g of BLENDEX BHPP 820 brand of poly(2,6-dimethylphenol), obtained from General Electric Specialty Chemicals, Parkersburg, WV, with gentle heating, in 90 g of toluene. The resulting PPO-toluene solution was then filtered through a 0.45 micron PTFE filter, was barcoated onto aluminum coupons with a #24 wire wound rod, and was baked for five minutes at 200° C in a forced air oven. After baking, the coupons were immersed in room temperature water and were then dried in air. Aluminum coupons which had been cleaned with solvent but not otherwise treated were also measured by the technique of the present invention.

In the DC potentiodynamic technique described earlier, the coated aluminum coupon was made the working electrode of an electrochemical cell. A graphite rod was the counter

electrode; a saturated calomel electrode (SCE) was the reference. Increasingly positive potentials were imposed on the working electrode, and current density between working and counter electrodes was measured. Low current density in the region of 0 to +1 V vs. SCE was judged as evidence of a diminished tendency to corrosion. Any abrupt increase in current density at relatively positive applied voltages was correlated to pitting of the metal surface; pits formed in this way could be seen without magnification. The high current density at relatively low applied voltage was further correlated to extensive pitting.

Current-voltage plots were generated for samples: (A); an aluminum coupon with no polymer coating; and (B), aluminum with a poly(2,6-dimethylphenol) coating, film thickness under 0.1 mil. The data indicated in two ways that poly(2,6-dimethylphenol) afforded pitting protection to the substrate metal: the current density in the entire applied voltage region (-1.5 to +1 V vs. SCE) was about two orders of magnitude lower, and (ii) in the region -0.5 to +1.0 there was no abrupt increase in current density in the coated sample as there was evident in the spectrum of the uncoated sample. Inspection of the coupons after testing confirmed the spectra: pits were clearly evident in the uncoated coupon but were not evident in the coated coupon.

Example 2

In this Example, cold rolled steel (CRS) was coated with a clear or pigmented epoxy-melamine coating and measurement of the DC current-voltage behavior was measured.

ACT cut only unpolished cold rolled steel coupons were cleaned of shop oil and grit with acetone and MEK scrubbing. Epoxy-melamine primer paints suitable for coating on a steel substrate were prepared in the following manner: bases of various "pigments", including Monsanto VERSICON brand polyaniline emeraldine base ("PANI-EB") and General Electric

BLENDEX BHPP 820 brand poly(2,6-dimethylphenol) ("PPO") were ground; were then dispersed, using a high speed sand grind mixer, in a 40% solids solution of an advanced, 9-type epoxy resin (Akzo Nobel HV 6156 brand). Then, MEK and A-100 solvents were added, as needed, to ensure formation of homogeneous dispersions. Typically, 41.6 g of "pigment" was added to 208 g of epoxy resin solution, to which 97.7 g of A-100 and 14.3 g of MEK solvents were added. Aliquots of the various grind bases were taken and diluted with epoxy resin solution and with CYMEL 380 brand melamine solution to form pigment:binder concentrations ("p/b") of 0.44, 0.22, and 0.15 on a weight basis. In addition, samples were prepared from unpigmented or "clear" epoxy-melamine solution and from strontium chromated pigmented epoxy-melamine (Akzo Nobel 9X444 brand).

The paint formulations described above were applied to the cleaned steel substrate with a #14 wire wound rod, the resulting samples were then baked to a 420°F peak metal temperature, and they were then quenched by immersion in tap water.

Using the DC potentiodynamic technique of this invention, each coated steel coupon was again made the working electrode of an electrochemical cell, with a graphite rod counter electrode, and a saturated calomel electrode reference. Each coating was scored in the region of measurement with a knife-edge, forming an "X" (1.5 cm for each score) to expose the bare metal. In this testing, 0.1 N NaHCO₃ was the electrolyte. In the course of measurement, increasingly positive potentials were imposed on the working electrode, and the current density between the working and counter electrodes was measured. Low current density in the region of 0 to +1 V vs. SCE was taken as evidence of diminished tendency of the sample to corrode.

Current-voltage plots were generated for samples: (C), steel with clear epoxy-melamine primer; (D), steel coated with chromated epoxy-melamine primer; (E), steel coated with epoxy

melamine and PPO pigment; (F), steel coated with epoxy melamine and PANI-EB pigment; and (G), steel coated with epoxy melamine and VERSICON pigment.

The data indicated in two ways that various pigments afford corrosion protection to the substrate steel: the open circuit potential of the unpigmented coated sample (C) was relatively negative (-0.70 V), and the current density in the region 0 to $+1$ V vs. SCE was high (about 10^{-3} A/cm²); the chromate-coated sample had a relatively positive open circuit potential (-0.45 V) and low current density (about 10^{-6} A/cm²); samples coated with either PPO (E) or PANI-EB (F) pigmented epoxy-melamine showed an active-passive transition at an applied voltage of about -0.4 V and a passive region of low current density (about 10^{-5} A/cm²) in the region 0 to $+1$ V of applied voltage. The sample coated with the VERSICON brand pigment (G) did show an active-passive transition at about -0.3 V but had a rather high current density (about 10^{-3} A/cm²) in the passive region.

The forgoing Examples, since they merely illustrate certain embodiments of the present invention, should not be used to construe the present invention in a limiting fashion. The scope of protection sought is set forth in the Claims which follow.

I Claim:

1. An electrochemical test method for determining the resistance to corrosion of a metal article coated with a
5 resinous coating which comprises:

(a) making a portion of the coated metal article, from which a portion of the coating has been removed to allow for the ultimate passage of electrical current therethrough, the working electrode in an electrochemical cell which also
10 contains a reference electrode, a counter-electrode and an electrolytic solution;

(b) impressing a series of direct current electrical potentials upon the working electrode to enable current to flow between the metal article in the
15 electrochemical cell and the counter-electrode; and

(c) measuring the current flow as the direct current potential is varied relative to the reference electrode.

20 2. A method as claimed in Claim 1 wherein the resinous comprises at least one corrosion inhibiting additive.

25 3. A method as claimed in Claim 1 wherein the metal is steel.

4. A method as claimed in Claim 1 wherein the resinous comprises at least one corrosion inhibiting additive and the metal is steel.

30 5. A method as claimed in Claim 1 wherein the reference electrode is a saturated calomel electrode.

35 6. A method as claimed in Claim 1 wherein the counter-electrode comprises graphite and the reference electrode is a saturated calomel electrode.

7. A method as claimed in Claim 1 wherein the reference electrode is a saturated calomel electrode, the working electrode comprises coated steel, and the counter-electrode
5 comprises graphite.

8. A method as claimed in Claim 1 wherein the resinous coating comprises at least one corrosion inhibiting additive, the reference electrode is a saturated calomel electrode, the
10 working electrode comprises coated steel, and the counter-electrode comprises graphite.

9. A method as claimed in Claim 1 wherein the metal is steel, the reference electrode is a saturated calomel
15 electrode, the working electrode comprises coated steel, and the counter-electrode comprises graphite.

10. A method as claimed in Claim 1 wherein the resinous coating comprises at least one corrosion inhibiting additive, the metal is steel, the reference electrode is a saturated
20 calomel electrode, the working electrode comprises coated steel, and the counter-electrode comprises graphite.

11. A method as claimed in Claim 1 wherein the metal is
25 aluminum.

12. A method as claimed in Claim 1 wherein the metal is aluminum, the working electrode comprises coated aluminum and the counter-electrode is selected from the group consisting of
30 graphite and platinum.

13. A method as claimed in Claim 1 wherein the resinous comprises at least one corrosion inhibiting additive, the metal is aluminum, the working electrode comprises coated

aluminum and the counter-electrode is selected from the group consisting of graphite and platinum.

1/2

Fig. 1

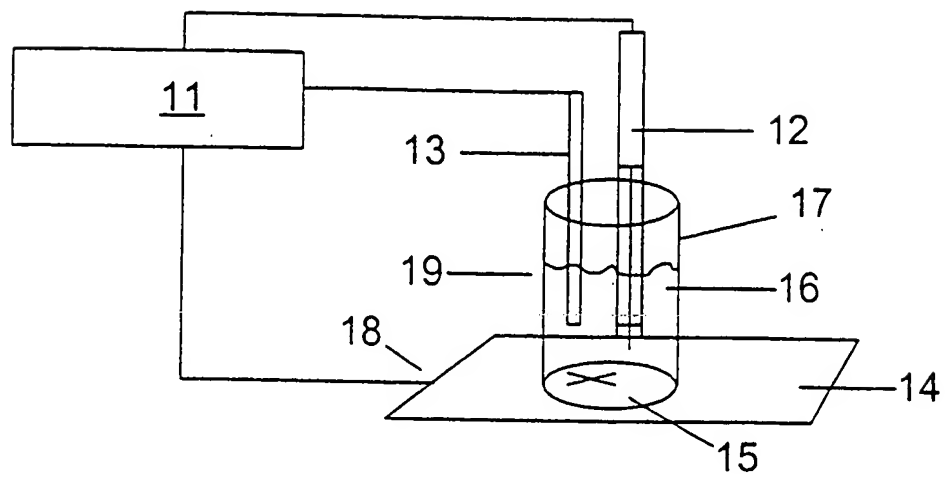


Fig. 2

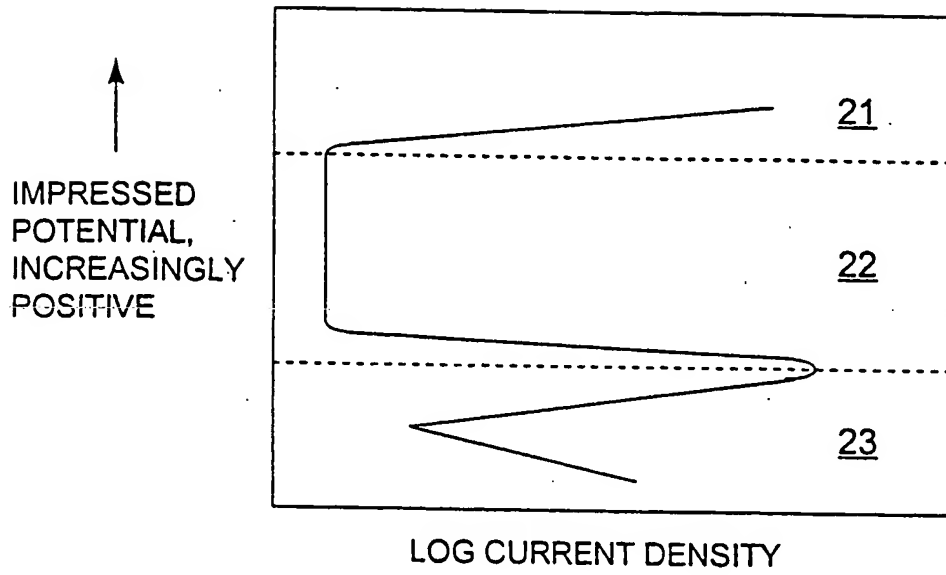
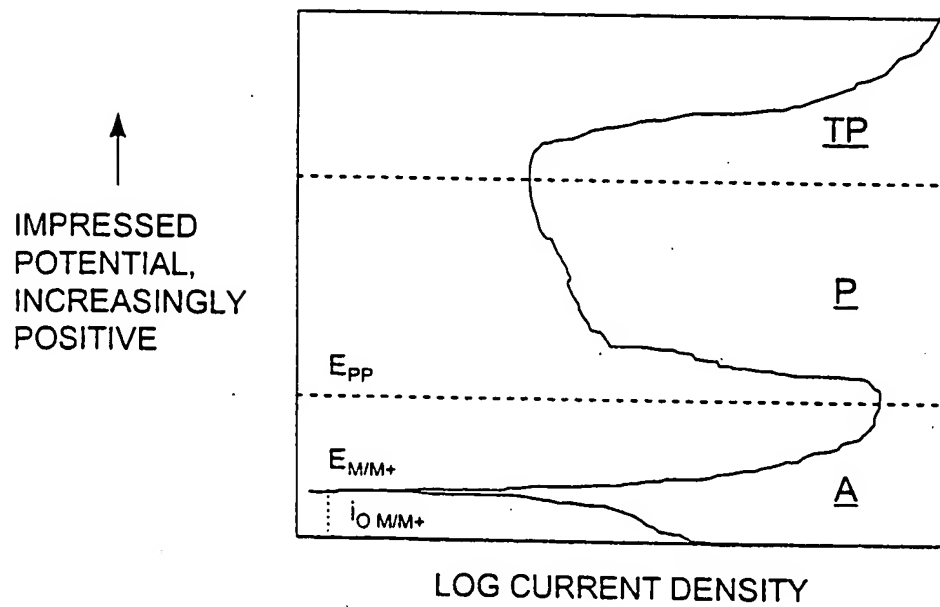


Fig. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/09766

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G01N 27/26

US CL :205/776.5

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/404; 205/775.5, 776, 776.5, 777, 791

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,406,101 A (KILPATRICK) 15 October 1968 (15-10-68), see column 3, line 29 to column 7, line 24.	1-13
Y	US 3,716,460 A (WEISSTUCH ET AL) 13 February 1973 (13-02-73), see column 3, line 59 to column 5, line 24.	1-13
Y	US 4,095,176 A (MAES ET AL) 13 June 1978 (13-06-78), see column 2, lines 25-32.	4, 10, 13
Y	US 4,294,667 A (YAMAMOTO ET AL) 13 October 1981 (13-10-81), see column 3, lines 16-50; column 9, line 28 to column 11, line 26, column 30, lines 26-37.	1-13
Y	US 4,515,643 A (KNASTER) 07 May 1985 (07-05-85), see column 2, lines 23-42.	1-13

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Date of the actual completion of the international search

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,863,571 A (CHAMBAERE) 05 September 1989 (05-09-89), see column 1, lines 4-24; column 2, lines 40-59.	1-13